

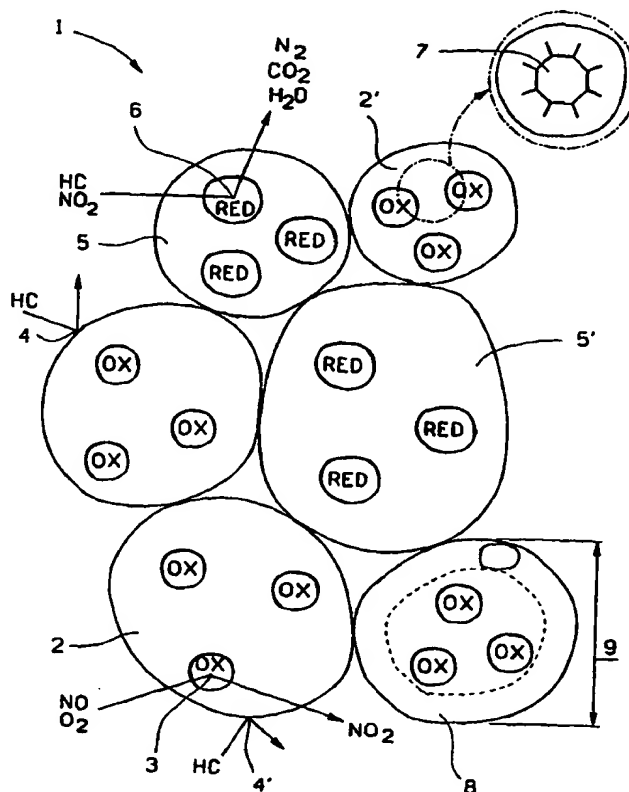
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/SE97/02067</p> <p>(22) International Filing Date: 10 December 1997 (10.12.97)</p> <p>(71) Applicant (for all designated States except US): AB VOLVO [SE/SE]; S-405 08 Göteborg (SE).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): JOBSON, Edward [SE/SE]; Jägarevägen 5, S-442 77 Romelanda (SE). MARTENS, Johan, A. [BE/BE]; Borheidestraat 25, B-3040 Huldenberg (BE). CAUVEL, Anne [FR/FR]; 8, rue de la Gloriette, F-34230 Adissan (FR). JAYAT, François [FR/FR]; Cerceville, F-16170 Genac (FR).</p> <p>(74) Agents: GRAUDUMS, Valdis et al.; Albiñ West AB, P.O. Box 142, S-401 22 Göteborg (SE).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report.</p>

(54) Title: POROUS MATERIAL, METHOD AND ARRANGEMENT FOR CATALYTIC CONVERSION OF EXHAUST GASES

## (57) Abstract

The invention pertains to a porous material for catalytic conversion of exhaust gases, comprising an oxidation catalyst able to catalyse oxidation of nitrogen monoxide into nitrogen dioxide and to catalyse oxidation of a reducing agent. According to the invention, the oxidation of the reducing agent is prevented since the reducing agent is sterically prevented from coming into contact with the oxidation catalyst. Preferably, the porous material also comprises a carrier with a reduction catalyst having the ability to selectively catalyse reduction of nitrogen dioxide into nitrogen, whereby the reducing agent is at least partially consumed. The invention also relates to a method and an arrangement which utilize the porous material, and an advantageous use of the porous material. The invention may be applied within the field of catalytic conversion of exhaust gases, originating from internal combustion engines, particularly Lean Combustion engines and diesel engines.



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POROUS MATERIAL, METHOD AND ARRANGEMENT FOR CATALYTIC  
CONVERSION OF EXHAUST GASES

5 TECHNICAL FIELD:

The invention pertains to a porous material for catalytic conversion of exhaust gases. The porous material comprises a carrier with a first porous structure, and an oxidation catalyst which in the presence of oxygen has the ability to catalyse oxidation of nitrogen monoxide into nitrogen dioxide. The oxidation catalyst in itself also has the ability to catalyse oxidation of a reducing agent but, according to the invention, the oxidation of the reducing agent is prevented by means of the oxidation catalyst being enclosed inside the first porous structure, which has such dimensions that the reducing agent is sterically prevented from coming into contact with the oxidation catalyst.

20 Preferably, the porous material also comprises a carrier with a second porous structure and a reduction catalyst, which in the presence of the reducing agent is able to selectively catalyse reduction of nitrogen dioxide into nitrogen, whereby the reducing agent is at least partially consumed. The reduction catalyst is thereby located in the second porous structure which has such dimensions that the reducing agent can come into contact with the reduction catalyst. The invention also relates to a method and an arrangement which utilize the porous material, and indicates an advantageous use of the porous material.

The invention may be applied within the field of catalytic conversion of exhaust gases which originate from internal combustion engines, particularly Lean Combustion engines (LC-engines) and diesel engines.

The present invention may also be utilized for other exhaust gases, containing nitrogen oxides and having an oxygen surplus, which originate from stationary emission sources such as gas turbines, power plants and the like.

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#### BACKGROUND OF THE INVENTION:

When attempting to reduce the emissions of nitrogen oxides ( $\text{NO}_x$ ) from internal combustion engines, a lot of efforts have been made to modify the combustion conditions in order to reduce the  $\text{NO}_x$ -emissions, while still maintaining the combustion efficiency at a satisfactory level.

Amongst the traditional techniques for the reduction of  $\text{NO}_x$ -emissions may, inter alia, the technique of Exhaust Gas Recirculation (EGR) be mentioned, as well as special designs of fuel injectors and combustion chambers. Other important parameters are compression, fuel injection time and fuel injection pressure. Techniques involving water injection, the use of fuel/water emulsions and so-called Selective Catalytic Reduction (SCR) by ammonia, have also been employed. Thereby, it has been found that a one-sided optimization of the combustion efficiency often results in increased  $\text{NO}_x$ -emissions.

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Today, it is required that both the fuel consumption and the  $\text{NO}_x$ -emissions are reduced. There are also strong demands on reduced emissions of other chemical compounds which are potentially hazardous to the environment, e.g. hydrocarbons.

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Accordingly, there is an increased need for catalytic converters which also are able to treat exhaust gases from so-called Lean Combustion (LC) engines. Therefore, a number of different catalytic converters have been developed and

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are well-known from commercial applications in e.g. motor vehicles.

Typically, conventional catalytic converters comprise one or several matrices, or monolith bricks as they sometimes are called. Such bricks or monoliths are in the form of a ceramic honeycomb substrate, with through passages or cells, and can be furnished with a porous surface coating. Particles of a suitable catalyst are embedded in the surface of the matrix, and the design of the matrix has been optimized in order to maximise the surface area over which catalytic reactions take place. Common catalysts are noble metals, e.g. silver (Ag), platinum (Pt), palladium (Pd), rhodium (Rh), gallium (Ga) or ruthenium (Ru) or mixtures of these. There are also a number of other metals and metal oxides which may be used as catalysts. Such catalysts may have the ability to catalyse oxidation or reduction reactions, or both.

It is also previously known to use crystalline aluminium silicates, so-called zeolites, loaded with a suitable catalyst. The use of zeolites in connection with the catalytic conversion of exhaust gases is disclosed in e.g. EP 0 499 931 A1 and EP 0 445 408 A.

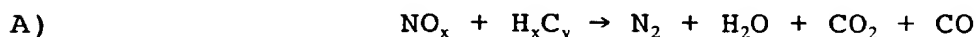
Furthermore, it is also previously known to combine several different catalytic matrices, or to arrange a so-called after-burner in the catalytic conversion process. Such arrangements are disclosed in e.g. U.S. Patent No. 5,465,574.

It is also previously known to use a honeycomb monolith of corrugated metal foil, having a suitable catalyst carried or supported on its surface.

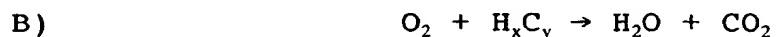
It has also been suggested, e.g. in EP 0 483 708 A1, to combine a conventional ceramic catalytic converter with an electrically heatable catalytic converter in order to ensure that the optimum temperature for catalytic conversion is maintained.

Thus, a number of different catalyst materials, devices, and arrangements for the catalytic conversion of exhaust gases have been described in the art.

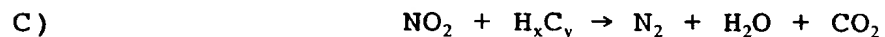
Thereby, it is believed that simultaneous elimination of nitrogen oxides ( $\text{NO}_x$ ) and hydrocarbons ( $\text{H}_x\text{C}_y$ ) may take place over e.g. an Ag-catalyst, according to the (simplified) chemical reactions:



and



However, in practice, it has been found that the following reaction is predominant:



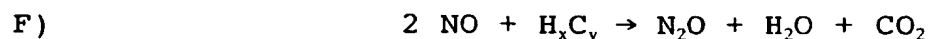
It should be noted that the term  $\text{H}_x\text{C}_y$  in the chemical reactions herein not only refers to hydrocarbons but is also relevant for other reducing agents which further comprise oxygen and/or sulphur. Accordingly, the reducing agent  $\text{H}_x\text{C}_y$  could also be expressed as  $\text{H}_x\text{C}_y\text{O}_z\text{S}_w$ . Examples of reducing agents which might be present in exhaust gases are alkanes, alkenes, paraffines, alcohols, aldehydes, ketones, ethers or esters and different sulphur-containing compounds. Also CO or  $\text{H}_2$  could act as reducing agents. The reducing agent in the exhaust gases can originate from the

fuel or the combustion air, or it can be added to the exhaust gases on purpose.

It has earlier been found that the above-mentioned reaction according to C) is very rapid over e.g. Ag-catalysts. Acidic catalysts ( $H^+$ ) and acidic zeolites, doped with Ag or other suitable catalysts, have been found to be selective in the sense that  $NO_2$  will readily be converted, whereas NO will not. This can be a great disadvantage since NO is predominant in "lean" exhaust gases from e.g. LC-engines. Another problem is that the available amount of  $NO_2$  can become limiting for the reduction of hydrocarbons ( $H_xC_y$ ) or other undesired compounds.

In order to solve this problem, i.e. to be able to reduce the amount of both NO and  $H_xC_y$  in the exhaust gases, it has earlier been suggested to combine an Ag-zeolite catalyst with a Pt-catalyst.

Normally, the following main reactions will take place over a conventional Pt-catalyst:



When using a conventional Ag-zeolite catalyst in combination with a conventional Pt-catalyst, all four reactions C), D), E) and F) will occur. However, since hydrocarbon ( $H_xC_y$ ) is consumed in the chemical reactions E) and F), there is a risk that there will not be a sufficient amount of hydrocarbon ( $H_xC_y$ ) left for the reaction with nitrogen dioxide ( $NO_2$ ), according to reaction C). This results in an undesired residue of nitrogen dioxide ( $NO_2$ )

in the catalytically converted exhaust gases, originating from reaction D).

Previous attempts have been made to solve this problem with different types of catalysts, by means of combining different catalysts, and by means of adding an additional amount of hydrocarbon to the exhaust gases in order to supply the reaction C) with a sufficient amount of hydrocarbon.

However, many of the previous solutions have been associated with the problem of undesired oxidation of hydrocarbons ( $H_xC_y$ ) over at least some surfaces of the oxidation catalyst, which preferably only should catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide ( $NO_2$ ), according to reaction D).

Another problem associated with many previously known catalysts is that, during certain conditions, they will catalyse reaction F) which produces dinitrogen oxide ( $N_2O$ ). This reaction is undesired and it is preferred that the nitrogen oxides ( $NO_x$ ) in the exhaust gases are converted into nitrogen ( $N_2$ ) to the highest possible degree, and not into dinitrogen oxide ( $N_2O$ ).

#### TECHNICAL PROBLEM:

Accordingly, there is a need for a new, selective oxidation catalyst material, which catalyses oxidation of nitrogen monoxide (NO) into nitrogen dioxide ( $NO_2$ ) and which does not catalyse oxidation of hydrocarbons.

Furthermore, there is also a need for an effective combination of such a selective oxidation catalyst material, catalysing a reaction which produces nitrogen dioxide ( $NO_2$ ), and a reduction catalyst material,



catalysing a reaction in which nitrogen dioxide ( $\text{NO}_2$ ) is reduced by hydrocarbons or other reducing agents into nitrogen ( $\text{N}_2$ ).

5 SUMMARY OF THE INVENTION:

Accordingly, a first object of the present invention is to provide a porous material for catalytic conversion of exhaust gases, by means of which porous material it is possible to selectively catalyse the oxidation of nitrogen  
10 monoxide ( $\text{NO}$ ) into nitrogen dioxide ( $\text{NO}_2$ ), and avoid catalytic oxidation of hydrocarbons ( $\text{H}_x\text{C}_y$ ) or other reducing agents.

15 This first object of the invention is achieved by means of a porous material for catalytic conversion of exhaust gases which, according to claim 1, comprises a carrier with a first porous structure, and an oxidation catalyst. In the presence of oxygen, the oxidation catalyst has the ability  
20 to catalyse oxidation of nitrogen monoxide into nitrogen dioxide, according to a first reaction. Furthermore, the oxidation catalyst in itself has the ability to catalyse oxidation of a reducing agent, according to a second reaction. According to the invention, the oxidation  
25 catalyst is enclosed inside the porous structure, which has such dimensions that the reducing agent is sterically prevented from coming into contact with the oxidation catalyst. This will enable primarily the first reaction, out of said first and second reactions, to take place over  
30 the oxidation catalyst during the catalytic conversion of the exhaust gases.

Furthermore, a second object of the present invention is to provide a porous material for catalytic conversion of  
35 exhaust gases, wherein primarily only the desired reactions take place, as a result of which the contents of  $\text{NO}$ ,  $\text{NO}_2$

and  $H_xC_y$  in the catalytically converted exhaust gases are effectively decreased, and the resulting conversion products primarily are  $N_2$ ,  $CO_2$  and  $H_2O$ , and not  $N_2O$ .

5 The second object of the invention is achieved by means of a porous material according to claim 1 which, in accordance with claim 2, further comprises a carrier with a second porous structure and a reduction catalyst. In the presence of a reducing agent, the reduction catalyst is able to  
10 selectively catalyse reduction of nitrogen dioxide into nitrogen, according to a third reaction, whereby the reducing agent participates in the third reaction and is at least partially consumed. Thereby, the reduction catalyst is located in the second porous structure, which has such  
15 dimensions that the reducing agent can come into contact with the reduction catalyst in order to enable the third reaction to take place.

20 A third object of the present invention is to provide a method for catalytic conversion of exhaust gases in which the porous material according to the invention is utilized.

The third object of the invention is achieved by means of a method for catalytic conversion of exhaust gases which,  
25 according to claim 23, comprises oxidation of nitrogen monoxide into nitrogen dioxide over an oxidation catalyst, according to a first reaction, whereby said oxidation catalyst also has the ability to, according to a second reaction, catalyse oxidation of a reducing agent. According  
30 to the invention, however, the reducing agent is sterically prevented from coming into contact with the oxidation catalyst, as a result of which primarily the first reaction, out of said first and second reactions, takes place over the oxidation catalyst.

A fourth object of the present invention is to indicate an advantageous use of the porous material according to the invention.

5 In accordance with the invention, the fourth object is achieved by the use of a porous material according to the invention, providing functions both for the oxidation of nitrogen monoxide into nitrogen dioxide and for the reduction of nitrogen dioxide into nitrogen, for catalytic  
10 conversion of exhaust gases which have an oxygen surplus.

Finally, a fifth object of the present invention is to provide an advantageous arrangement for catalytic conversion of exhaust gases, utilizing the porous material  
15 according to the invention.

In accordance with the invention, the fifth object of the invention is achieved by an arrangement, for catalytic conversion of exhaust gases from an internal combustion  
20 engine, comprising a porous material according to the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS:

25 In the following, the invention will be described in greater detail with reference to the attached drawings and graphs.

Fig. 1 shows a schematic view of a portion of a porous  
30 material according to the invention, also with an enlarged view seen from inside a pore in the porous material. The major chemical reactions which occur during the catalytic conversion of exhaust gases are also indicated.

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Fig. 2 schematically depicts an embodiment of the porous material according to the invention, with an enlarged detailed view of a portion of the porous material including a supporting substrate.

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Fig. 3A schematically shows an enlarged detailed view of a portion of the enlarged detailed view in Fig. 2, and depicts a variant of the porous material according to the invention, comprising a physical mixture of two different zeolite carriers.

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Fig. 3B schematically shows another enlarged detailed view of a portion of the enlarged detailed view in Fig. 2, and depicts another variant of the porous material according to the invention, comprising a layered structure of two different zeolite carriers.

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Fig. 3C schematically shows an alternative to the layered structure in Fig. 3B.

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Fig. 4A schematically shows an embodiment of a porous material according to the invention, having a first portion and a second portion.

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Fig. 4B schematically shows another embodiment of the invention, wherein the porous material according to the invention comprises two separate, different parts, intended to be used together in a single catalytic conversion process.

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Fig. 5 shows a schematic process diagram of an arrangement for catalytic conversion of exhaust gases according to the invention.

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Graph 1A shows results from a laboratory evaluation of a porous sample, comprising a physical mixture of Pt-Ferrierite and Ag-Ferrierite, when a linear hydrocarbon is supplied in the gas which is to be catalytically converted.

Graph 1B shows results from a laboratory evaluation of the same porous sample as in Graph 1A, but when a branched hydrocarbon is supplied in the gas which is to be catalytically converted.

Graph 2A shows results from a laboratory evaluation of a porous material according to the invention, comprising a physical mixture of Pt-Ferrierite and Ag-Mordenite, when a linear hydrocarbon is supplied in the gas which is to be catalytically converted.

Graph 2B shows results from a laboratory evaluation of the same porous material according to the invention as in Graph 2A, but when a branched hydrocarbon is supplied in the gas which is to be catalytically converted.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS:

In the following, a porous material according to the invention will be described with reference to the attached drawings.

The porous material 1 in Fig. 1 comprises a carrier with a first porous structure 2, 2'. An oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2'. In the presence of oxygen ( $O_2$ ), the oxidation catalyst (OX) has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide ( $NO_2$ ), according to a first reaction

3. Furthermore, the oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction (not present in Fig. 1).

5 According to the invention, however, such oxidation of the reducing agent according to the second reaction is not desired, since the reducing agent (HC) is more useful in a third reaction, as will become apparent below.

10 In order to prevent the undesired second reaction from occurring, the oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2', which has such dimensions that the reducing agent (HC) is sterically prevented 4, 4' from coming into contact with the oxidation catalyst (OX).  
15 This will enable primarily the desired first reaction 3, out of said first and second reactions, to take place over the oxidation catalyst (OX) during the catalytic conversion of exhaust gases. In this context, the term "first porous structure" primarily refers to internal micro-pores in the  
20 carrier material or micro-pores between carrier particles or grains.

Preferably, the porous material 1 further comprises a carrier with a second porous structure 5, 5', in which a  
25 reduction catalyst (RED) is located. In this context, the term "second porous structure" can include internal micro-pores in the carrier material, or cavities or channels between carrier particles, but also cavities inside or channels through the porous material, i.e. macro-pores. In  
30 the presence of a reducing agent (HC), the reduction catalyst (RED) is able to selectively catalyse reduction of nitrogen dioxide ( $\text{NO}_2$ ) into nitrogen ( $\text{N}_2$ ), according to a third reaction 6, shown schematically in Fig. 1. Thereby, the reducing agent (HC) participates in the third reaction  
35 6 and is at least partially consumed.

According to the invention, the reduction catalyst (RED) is located in the second porous structure 5, 5', which has such dimensions that the reducing agent (HC) can come into contact with the reduction catalyst (RED). This enables the  
5 desired third reaction 6 to take place during the catalytic conversion of exhaust gases.

According to one embodiment of the porous material according to the invention, the first porous structure 2,  
10 2' on an average exhibits smaller entrances 7 for the reducing agent (HC) than the second porous structure 5, 5'. In this way, the reducing agent (HC) is prevented from getting into contact with the oxidation catalyst (OX), enclosed inside the first porous structure 2, 2', but is  
15 not prevented from coming into contact with the reduction catalyst (RED) in the second porous structure 5, 5'. The pores in the first porous structure 2, 2' should preferably primarily have an effective size of 3-6 Å.

20 According to another embodiment of the porous material, both the first 2, 2' and the second 5, 5' porous structures are provided in the same layer or coating of the porous material.

25 If desired, however, the first 2, 2' and the second 5, 5' porous structures can be provided in different layers/coatings of the porous material. This might be an advantage, depending on the composition of the exhaust gases which are to be catalytically converted.

30 In one embodiment of the porous material, the carrier with the second porous structure 5, 5' is adapted to the molecule size and/or the adsorption properties of the reducing agent (HC) or agents, which is/are expected to  
35 occur in the exhaust gases.

In another embodiment of the porous material, the ratio between the oxidation catalyst (OX) and the reduction catalyst (RED) has been optimized so that the production of nitrogen dioxide ( $\text{NO}_2$ ), according to the first reaction 3, essentially corresponds to the consumption of nitrogen dioxide ( $\text{NO}_2$ ), according to the third reaction 6.

In still another embodiment of the invention (Fig. 4A), the porous material further comprises a first portion 10 and a second portion 11, wherein the first portion 10 is intended to receive exhaust gases 12 before the second portion 11 during the catalytic conversion. Thereby, the first portion 10 contains a larger quantity of the oxidation catalyst (OX) than the second portion 11, whereas the second portion 11 contains a larger quantity of the reduction catalyst (RED) than the first portion 10. Accordingly, in a flow of exhaust gases the first reaction 3, producing  $\text{NO}_2$ , will take place upstream the third reaction 6, which consumes  $\text{NO}_2$ . As shown in Fig. 4B, it is also conceivable with embodiments wherein the first and second portions are separated from each other, as long as they are used for catalytic conversion in the same conversion process.

According to one embodiment of the porous material, the first 2, 2' and/or the second 5, 5' porous structure is provided in a carrier which is a zeolite crystal structure.

Furthermore, both the first 2, 2' and the second 5, 5' porous structures can be provided in carriers of zeolite type, wherein preferably the first porous structure 2, 2' is provided in a first zeolite 14 and the second porous structure in a second zeolite 15.

As earlier mentioned, according to the invention, the first porous structure 2, 2' and, accordingly, also the first zeolite 14 should provide suitable properties in order to



prevent the earlier-mentioned, undesired second reaction from taking place.

There are a number of different ways of combining different zeolites in a porous material according to the invention. Accordingly, the porous material can comprise a physical mixture 13 of the first zeolite 14 and the second zeolite 15 (Fig. 3A).

Furthermore, the porous material can comprise a layered structure 16, 17 of the first zeolite and the second zeolite (Figs. 3B and 3C). Different layers may also be applied or coated onto different supporting substrates 18 or different surfaces of a substrate 18.

In certain applications, it may be preferred to arrange the layered structure 17 so that, in a flow of exhaust gases, the second zeolite will encounter the exhaust gases before the first zeolite. This might be the case e.g. when the exhaust gases which are to be converted contain a proportionately high content of NO<sub>2</sub> but a low content of NO.

In other applications, e.g. when the content of NO in the exhaust gases is proportionately high but the content of NO<sub>2</sub> is low, it might be desirable to arrange the layered structure 16 in the opposite way, i.e. the first zeolite outside the second zeolite.

According to one embodiment of the porous material, a layered structure is achieved by means of the second zeolite 15, which provides the second porous structure 5, 5', being crystallized onto the first zeolite 14, which provides the first porous structure 2, 2'. This can be done by means of so-called over-growth.

Another embodiment of the porous material aims at further reducing the occurrence of the earlier-mentioned, undesired second reaction. In this embodiment, the content of oxidation catalyst (OX) has been reduced in the outer layers 8 of the first zeolite by means of partial ion-exchange (indicated in Fig. 1). Methods for altering the penetration depth and dispersion of the catalytically active metals are well-known to the skilled person and will not be described in any greater detail.

In another embodiment of the porous material, an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) has been crystallized onto the first zeolite, by means of so-called over-growth. Thereby, the additional layer advantageously comprises a zeolite which provides a porous structure with even smaller pores/entrances than the first zeolite. In this way, undesired reducing agent can more effectively be prevented from getting inside the internal pore structure of the first zeolite, at the same time as the nitrogen oxide (NO) will be admitted and can move freely inside said internal pore structure.

Also the dimensions of the crystal grains in the zeolite crystal structures can be used in order to facilitate desired chemical reactions, and in order to prevent undesired chemical reactions. Different crystal structures can be achieved in several different ways, e.g. by means of the choice of the crystallization conditions and the choice of zeolite type. Also the internal pore structure of the zeolites is influenced by the choice of zeolite type.

Thus, according to one embodiment of the porous material, the size and shape of the crystal grains in the crystal structure of the first zeolite, has been optimized both in order to prevent access for the reducing agent (HC), and in order to allow oxidation of NO to NO<sub>2</sub>. The optimization of

the grain size is important since it makes it possible to maximise the oxidation of NO into NO<sub>2</sub>, and to minimize the oxidation of HC.

5 In another embodiment of the porous material, a proportionately small pore size, in the crystal structure of the first zeolite which provides the first porous structure 2, 2', has been achieved by means of selecting a Ferrierite-zeolite or a Chabazite-zeolite, and not e.g. a  
10 Mordenite-zeolite.

As earlier mentioned, the porous material according to the invention has the ability to catalyse oxidization of nitrogen monoxide (NO) into nitrogen dioxide (NO<sub>2</sub>), and  
15 preferably also the ability to selectively catalyse reduction of nitrogen dioxide (NO<sub>2</sub>) into nitrogen (N<sub>2</sub>) in the presence of a reducing agent (HC). Thereby, the reducing agent (HC) may be any suitable reducing agent which is present in, or added to, the exhaust gases which  
20 are to be catalytically converted.

It is an advantage, however, if the reducing agent (HC) in the exhaust gases is a hydrocarbon (H<sub>x</sub>C<sub>y</sub>) or a chemical compound comprising oxygen and sulphur (H<sub>x</sub>C<sub>y</sub>O<sub>z</sub>S<sub>w</sub>). These  
25 compounds can originate from the fuel which is combusted and will, as earlier mentioned, be at least partially consumed according to the earlier-mentioned third reaction 6 over the reduction catalyst (RED). Alternative fuels, e.g. rape methyl ether, may produce oxygen-containing  
30 compounds, whereas sulphur is frequently present in most fuels.

The reduction catalyst (RED) in the second porous structure 5, 5' might be of any suitable, previously known type.  
35 However, in the porous material according to the invention, the reduction catalyst (RED) preferably comprises Brönstedt

acid sites, and silver (Ag), copper (Cu) or Rhodium (Rh), Cobalt (Co), Indium (In), Iridium (Ir) or combinations of these. In the porous material according to the invention, acidic zeolite catalysts are preferred as reduction catalysts (RED) .

The oxidation catalyst (OX) may be of any type suitable for the purpose, but preferably comprises platinum (Pt) and/or Palladium (Pd).

The herein used term "porous material" should be regarded as including the entire structure/mass which might be present inside a unit for the catalytic conversion of exhaust gases. Accordingly, the term "porous" should be understood both in a microscopic and in a macroscopic sense, i.e. the porous material could comprise elements which in themselves are not porous to exhaust gases. However, the material structure as a whole, i.e. the "porous material" according to the invention, will allow the exhaust gases which are to be catalytically converted to pass through. It should also be noted that embodiments wherein the porous material is composed of several separated parts, having different structures and functions, are conceivable, as long as they are used in the same catalytic conversion process.

The porous material, according to the invention, may be coated onto one or several suitable substrates or matrixes in order to provide a carrier or several carriers which comprise the first or/and the second porous structures. Suitable substrates for this purpose are well-known from the prior art, and will not be described in any greater detail, especially since they are of minor importance for the invention.

Accordingly, the substrate 18 may be a metal substrate of a previously known type. The substrate 18 may also be a supporting, previously known, honeycomb structure of a suitable material, with or without catalytic activity.

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It should also be noted that the term "porous structure" used herein should be understood as to include both micro-pores and macro-pores of the porous material. Accordingly, internal micro-pores, cavities between carrier particles, channels inside or through the porous material, etc., are all included within the scope of "porous structure".

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For instance, there is no need for the second porous structure 5, 5 to be an internal micro-pore structure inside a carrier material, but the second porous structure 5, 5' could instead be provided by a more open, macroscopic structure. The first porous structure 2, 2', however, is preferably an internal micro-structure inside a carrier material, in order to provide sufficient sterical hindrance against the admittance of the (undesired) reducing agent into the sites where the oxidation catalyst is situated.

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In the following, a method for catalytic conversion of exhaust gases, according to the invention, will be described in greater detail with reference to the attached Figs. 1 and 5. The method according to the invention comprises oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO<sub>2</sub>) over an oxidation catalyst (OX), according to a first reaction 3 (Fig. 1). The oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction (not present in Fig. 1). According to the invention, however, the reducing agent (HC) is sterically prevented 4, 4' from coming into contact with the oxidation catalyst (OX). As a result of this, primarily the first reaction 3, out of said first and

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second reactions, takes place over the oxidation catalyst (OX).

According to one embodiment of the invention, the method further comprises reduction of nitrogen dioxide ( $\text{NO}_2$ ) into nitrogen ( $\text{N}_2$ ) over a reduction catalyst (RED) in the presence of a reducing agent (HC), according to a third reaction 6. Thereby, the reducing agent (HC) participates in the third reaction 6 and is at least partially consumed. In this way, catalytically converted exhaust gases 12' (Fig. 5), having a reduced content of nitrogen monoxide (NO), nitrogen dioxide ( $\text{NO}_2$ ) and reducing agent (HC) and a proportionately low content of dinitrogen oxide ( $\text{N}_2\text{O}$ ), are obtained. Furthermore, the converted exhaust gases will have a reduced content of carbon monoxide (CO).

When desirable, an additional amount 19, 19', 19'' of reducing agent (HC) can be added with a suitable injection device 28, before reduction takes place over the reduction catalyst (RED), according to the third reaction 6 (Figs. 1 and 5). In this way, the stoichiometrics of the occurring chemical reactions can be influenced so that the catalytic conversion becomes as complete as possible. In internal combustion engines, it is also possible to increase or regulate the amount of available reducing agent by means of so-called engine parameter tuning. This can be done by e.g. fuel injection timing, valve timing, post-injection, control of charging pressure and/or fuel injection pressure, EGR, transmission ratio, etc.

Advantageously, the additional amount 19, 19', 19'' of reducing agent (HC) can be regulated on the basis of a measured or previously mapped content 20 of reducing agent (HC) and/or nitrogen oxides ( $\text{NO}_x$ ) in the exhaust gases 12, 12'.

The measured content 20 of reducing agent (HC) or nitrogen oxides ( $\text{NO}_x$ ) in the catalytically converted exhaust gases (12') can also be used in a diagnostic control system 22, providing an indication of the status of the catalytic conversion.

The exhaust gases 12 can also be passed through a device having the ability to store and when necessary release nitrogen oxides ( $\text{NO}_x$ ) before the oxidation over the oxidation catalyst (OX), according to the first reaction 3. Such  $\text{NO}_x$ -absorbers are well-known to the person skilled in the art, and will not be described in any greater detail herein. Before the oxidation, the exhaust gases 12 can also be passed through a previously known device having the ability to store, and when necessary release, reducing agent (HC), e.g. hydrocarbon. This embodiment is useful for e.g. cold starts of an internal combustion engine.

In order to ensure that the oxidation catalyst (OX) and/or the reduction catalyst (RED) is functioning in the best possible way, i.e. are within an active temperature interval, the temperature of the exhaust gases can be regulated before the passage through the porous material 21 according to the invention. This can be done with any previously known device 23 which is suitable for the purpose.

In order to further improve the catalytic conversion, the exhaust gases can be allowed to pass a second oxidation catalyst 24, over which oxidation of residues of reducing agent and/or carbon monoxide can take place. In this way, it is ensured that the exhaust gases, which have been at least partially catalytically converted over the porous material 21, reach a sufficiently high degree of catalytic conversion.

It is advantageous for the method of the invention if the exhaust gases 12 originate from an internal combustion engine 25, and the reducing agent (HC) comprises a hydrocarbon ( $H_xC_y$ ) and/or a chemical compound ( $H_xC_yO_zS_w$ ) further comprising oxygen and/or sulphur.

Furthermore, the fuel 26 consumption of the internal combustion engine 25 will influence the chemical composition of the exhaust gases 12. Legislative regulations are imposed both on fuel consumption and the residue content of nitrogen oxides ( $NO_x$ ) in the catalytically converted exhaust gases 12'. In one embodiment of the invention, both the fuel consumption of the internal combustion engine, and the residue content of nitrogen oxides ( $NO_x$ ) in the catalytically converted exhaust gases 12', are regulated in order to fulfil the relevant legislative regulations.

In one preferred embodiment of the method according to the invention, the internal combustion engine 25 is a diesel engine and the reducing agent (HC) originates from internal combustion in said diesel engine.

When diesel engines are concerned, an additional amount 19 of reducing agent (HC) can advantageously be supplied to the engine via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

It is preferred to use a porous material according to the invention, for catalytic conversion of exhaust gases 12, which have an oxygen surplus and, accordingly, are difficult to convert in conventional catalytic converters, e.g. three-way converters. In such use, the porous material provides functions both for the oxidation of nitrogen monoxide (NO) into nitrogen dioxide ( $NO_2$ ) and for the reduction of nitrogen dioxide ( $NO_2$ ) into nitrogen ( $N_2$ ).



It is also preferred with an arrangement 27, according to the invention, for catalytic conversion of exhaust gases which originate from an internal combustion engine 25. Thereby, the arrangement comprises a porous material 21 according to the invention or, furthermore, operates through a method according to the invention.

EXAMPLE:

In order to more clearly illustrate the basic principles of the present invention, a number of porous samples, i.e. model catalyst materials, were produced in a series of laboratory trials.

In the laboratory trials, zeolites of the basic types Mordenite, Ferrierite and Chabazite were used in order to provide catalyst carriers.

The different zeolite types had the following channel/pore dimensions:

Mordenite:        free diameter: 12 rings 6.5 x 7.0 Å  
                     8 rings 2.6 x 5.7 Å

Ferrierite:       free diameter: 10 rings 4.2 x 5.4 Å  
                     8 rings 3.5 x 4.8 Å

Chabazite:        free diameter: 8 rings 3.8 x 3.8 Å

As evident from above, the selected zeolites had either 8 rings, 10 rings or 12 rings, providing entrances into their internal micro-pore structure. The selected zeolite raw materials were provided in the form of NH<sub>4</sub>-zeolites.

### Preparation of platinum-zeolites (Pt)

Samples of the different  $\text{NH}_4$ -zeolites were calcined during 1 h at 500 °C under oxygen flow in order to transfer the zeolites into acidic form, i.e into H-zeolites. Amounts of 0.5 wt-%, 1.0 wt-% or 1.5 wt-% of platinum (PT) were loaded onto the H-zeolites by means of contacting them with an aqueous solution of  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ . Thereby, the 0.01 M Pt-solution was added dropwisely to zeolite dispersed in water. The obtained mixtures were stirred during 24 h at room temperature, filtered, washed with  $\text{H}_2\text{O}$ , and dried overnight at 60 °C. Thereafter, the samples were calcined during 2 h at 450 °C in dry air, with a rate of 0.5 °C x  $\text{min}^{-1}$ , whereafter the samples were cooled down in a  $\text{N}_2$ -flow.

Methods for Pt-loading are described in greater detail in the publications J. Catal. 113 (1988), p. 220-235 (Tzou et al.) and J. Catal. 117 (1989), p. 91-101 (Homeyer et al.).

### Preparation of silver-zeolite (Ag)

Ag-zeolites were produced by loading 5 wt-% Ag onto the different  $\text{NH}_4$ -zeolites by means of impregnation with  $\text{AgNO}_3$ , using the so-called "incipient wetness" method. Thereby, the metal salt ( $\text{AgNO}_3$ ) was dissolved in a minimum of water (1 ml/gram of zeolite), whereafter the obtained solution was mixed with the zeolite powders. Finally, the samples were calcined during 16 h at 550 °C in a muffle furnace and stored in the dark until evaluation took place.

### Evaluation of catalytic conversion efficiency

Before the evaluation, the obtained Pt-zeolites and Ag-zeolites, and physical mixtures of these, were compressed into pellets, i.e. model porous samples, and the catalytic

conversion efficiency of the different porous samples was evaluated.

In the prepared porous samples, the Pt-zeolites were intended to provide the earlier-mentioned NO-oxidation function, whereas the Ag-zeolites were intended to provide the earlier-mentioned NO<sub>2</sub>-reduction function.

The evaluation of the catalytic conversion efficiency was performed by means of inserting a small amount (0.3 ml) of porous sample, into a device suitable for the purpose of evaluating catalytic conversion efficiency. Thereafter, a gas flow of 300 ml/min, with the composition 500 ppm NO, 350 ppm C<sub>8</sub>H<sub>18</sub>, 6% O<sub>2</sub>, 12% H<sub>2</sub>O, 10% CO<sub>2</sub> and 350 ppm CO, was passed through the sample chamber in which the porous material sample was placed. The temperature was step-wisely increased from 140 till 500 °C, while the composition of the catalytically converted exhaust gases from the sample chamber was detected.

The catalytic conversion efficiency for some of the different porous samples, comprising the different zeolites and physical mixtures of these, is evident from Table 1 below. Table 1 lists the temperature at which the maximum conversion of NO to N<sub>2</sub> was obtained, the total NO<sub>x</sub>-conversion at this temperature, and the formation of N<sub>2</sub> and N<sub>2</sub>O, respectively, at this temperature. It should be noted that conversion into N<sub>2</sub> is desired in this case, while conversion into N<sub>2</sub>O is undesired.

Table 1

SAMPLE	T (°C)max. N <sub>2</sub> conv.	% NO <sub>x</sub> conv.	% formation	
			N <sub>2</sub>	N <sub>2</sub> O
1 wt% Pt-CHA 30% 5 wt% Ag-MOR 70%	280	44	32	12
1.5 wt% Pt-MOR 30% 5 wt% Ag-CHA 70%	220	100	19	81
1 wt% Pt-MOR 100%	200	100	29	71
1 wt% Pt-CHA 100%	260	16	3	9
5 wt% Ag-CHA 100%	500	37	35	2

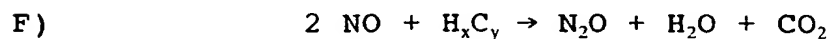
The results in Table 1 indicate that the highest total NO<sub>x</sub>-conversion will be achieved with porous samples comprising zeolites of Pt-Mordenite type. However, the strong formation of dinitrogen oxide (N<sub>2</sub>O) with Pt-Mordenite is a draw-back. The combined Pt-CHA/Ag-MOR sample exhibited very high conversion of NO<sub>x</sub> into N<sub>2</sub>. Also the Ag-CHA sample exhibited a high conversions of NO<sub>2</sub> to N<sub>2</sub> but only at a very high temperature (500 °C), which is impractical for many applications.

In Table 2 below, the catalytic conversion efficiency from further evaluations of different zeolites, and physical mixtures of these, are listed. The catalytic conversion efficiency is listed both for the case when the hydrocarbon (C<sub>8</sub>H<sub>18</sub>) in the supplied gas mixture is a linear alkane, i.e. n-octane, and for the case when the hydrocarbon (C<sub>8</sub>H<sub>18</sub>) is a strongly branched iso-paraffine, i.e. iso-octane (more specifically 2,2,4-tri-methylpentane).

Table 2

SAMPLE	T(°C) max. N <sub>2</sub> conv.	% NO <sub>x</sub> conv.		% formation			
		n-	iso-	N <sub>2</sub> n- C <sub>8</sub> H <sub>18</sub>	N <sub>2</sub> O iso- C <sub>8</sub> H <sub>18</sub>	n- C <sub>8</sub> H <sub>18</sub>	iso- C <sub>8</sub> H <sub>18</sub>
0.5 wt% Pt-FER 30% 5 wt% Ag-FER 70%	280	32	19	8	4	24	15
1.5 wt% Pt-MOR 20% 5 wt% Ag-FER 80%	260	30	32	4	8	26	24
0.5 wt% Pt-FER 30% 5 wt% Ag-MOR 70%	260	56	86	23	58	33	28
0.5 wt% Pt-FER 100%	240	62	16	15	9	47	7
5 wt% Ag-MOR 100%	360	15	15	13	13	2	2

As is evident from Table 2, the sample comprising Pt-Ferrierite alone (Pt-FER) provided a very high total NO<sub>x</sub>-conversion when the supplied hydrocarbon is a linear hydrocarbon, i.e. n-octane. This is a result from reaction of the linear hydrocarbon over the Pt-catalyst, according to the earlier mentioned reaction F):



As a result of this reaction, the formation of undesired dinitrogen oxide N<sub>2</sub>O is very high when supplying the linear hydrocarbon.

When instead the strongly branched iso-octane was supplied to the Pt-FER sample, the total NO<sub>x</sub>-conversion dropped drastically. The reason for this is that the strongly

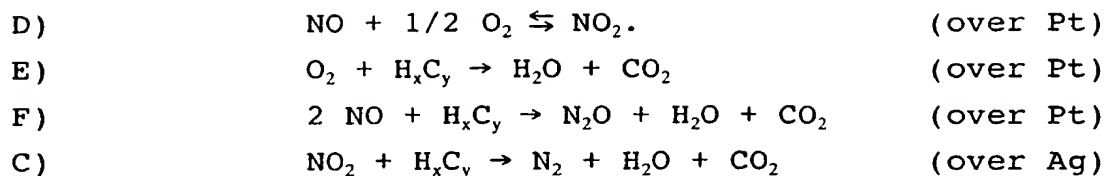
branched iso-octane is sterically prevented from coming into contact with the Pt-catalyst, because of the rather small entrances into the internal pore structure of the Pt-Ferrierite, inside of which the main portion of the Pt-catalyst is located. The linear hydrocarbon, on the other hand, is not sterically prevented from coming into contact with the Pt-catalyst in the internal pore structure, and therefore reaction F) can take place and consume NO.

As is also evident from Table 2, the porous sample comprising Ag-Mordenite alone provides a fairly low total NO<sub>x</sub>-conversion, and there is no difference in conversion efficiency when supplying n-octane and iso-octane, respectively. This result indicates that the strongly branched iso-octane is not sterically prevented from coming into contact with the Ag-catalyst to any higher extent than the linear n-octane. The reason for the low total NO<sub>x</sub>-conversion in this case is that the amount of nitrogen dioxide (NO<sub>2</sub>) in the test gas is too small to allow the earlier mentioned reaction C) to take place over the Ag-catalyst:



From these results, it can be concluded that Ferrierite-zeolites will admit linear hydrocarbons into their internal pore structure, but will not admit strongly branched hydrocarbons. Furthermore, it can be concluded that Mordenite-zeolites will admit both linear and strongly branched hydrocarbons into their internal pore structure.

Accordingly, a mixture of Pt-Ferrierite and Ag-Ferrierite should admit linear hydrocarbons, e.g. n-octane, and allow the four following reactions to take place over the combined Pt/Ag-catalyst sample:



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When the branched iso-octane is supplied instead, there will be less reaction according to reactions E), F) and C), since the branched iso-octane is at least partially sterically prevented from participating. The result of this is that the total  $\text{NO}_x$ -conversion drops, when supplying the branched iso-octane, as is evident from Table 2 (Pt-FER/Ag-FER). This is further illustrated by the attached Graphs 1A and 1B.

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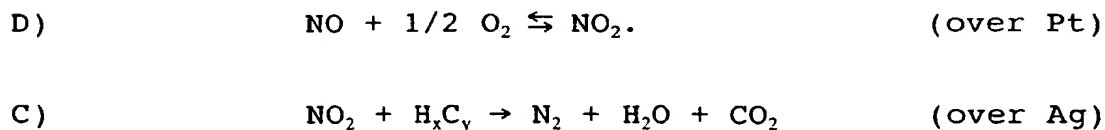
When using a porous material comprising a combination of Pt-Ferrierite and Ag-Mordenite (Pt-FER/Ag-MOR), the linear n-octane will have access into the internal pore structures of both the Pt-Ferrierite and the Ag-Mordenite. Accordingly, all four reactions D, E, F and C can take place. This results in a rather high total  $\text{NO}_x$ -conversion when supplying linear n-octane, as can be seen from the results in Table 2.

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As earlier discussed, the branched iso-octane is sterically prevented from getting into the pore structure of a Ferrierite-zeolite, but is not prevented from getting into the pore structure of a Mordenite-zeolite. Accordingly, when a branched hydrocarbon, e.g. iso-octane, is supplied to the physical mixture of Pt-Ferrierite and Ag-Mordenite, the reactions D and C will be predominant:

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This is indicated in Table 2 (Pt-FER/Ag-MOR) as a surprising increase of the total NO<sub>x</sub>-conversion, and a pronounced decrease of the relative N<sub>2</sub>O-formation, when the branched iso-octane is supplied instead of the linear n-octane. This effect is very useful for improving the catalytic conversion efficiency, and is further illustrated in the attached Graphs 2A and 2B.

Consequently, according to the invention, it is an advantage to sterically prevent hydrocarbons, or other reducing agents, from being oxidized according to reactions E) and/or F). A number of further conclusions can be drawn from this fact. This is also the basic principle which the present invention relies upon, as already has become evident from the earlier description.

The present invention should not be regarded as being limited to the herein described embodiments, but a number of further variants and modifications are conceivable within the scope of the following claims.



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## CLAIMS:

1. Porous material for catalytic conversion of exhaust  
10 gases, said porous material (1) comprising a carrier with  
a first porous structure (2, 2'), and an oxidation catalyst  
(OX) which in the presence of oxygen ( $O_2$ ), according to a  
first reaction (3), has the ability to catalyse oxidation  
15 of nitrogen monoxide (NO) into nitrogen dioxide ( $NO_2$ ) and,  
according to a second reaction, to catalyse oxidation of a  
reducing agent (HC),

c h a r a c t e r i z e d i n that the oxidation catalyst  
(OX) is enclosed inside the first porous structure (2, 2'),  
which has such dimensions that the reducing agent (HC) is  
20 sterically prevented (4, 4') from coming into contact with  
the oxidation catalyst (OX), in order to enable primarily  
the first reaction (3), out of said first and second  
reactions, to take place over the oxidation catalyst (OX)  
during the catalytic conversion of the exhaust gases.

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2. Porous material for catalytic conversion of exhaust  
gases according to claim 1, said porous material (1)  
further comprising a carrier with a second porous structure  
(5, 5') and a reduction catalyst (RED), which in the  
30 presence of the reducing agent (HC) is able to selectively  
catalyse reduction of nitrogen dioxide ( $NO_2$ ) into nitrogen  
( $N_2$ ), according to a third reaction (6), whereby the  
reducing agent (HC) participates in the third reaction (6)  
and is at least partially consumed,

35 c h a r a c t e r i z e d i n that the reduction catalyst  
(RED) is located in the second porous structure (5, 5'),  
which has such dimensions that the reducing agent (HC) can  
come into contact with the reduction catalyst (RED) in  
order to enable the third reaction (6) to take place.

3. Porous material for catalytic conversion of exhaust gases according to claim 2, characterized in that the first porous structure (2, 2') on an average exhibits smaller entrances (7) for the reducing agent (HC) than the second porous structure (5, 5'), and preferably that the first porous structure primarily comprises pores having an effective size of 3-6 Å.

4. Porous material for catalytic conversion of exhaust gases according to claim 2 or 3, characterized in that both the first (2, 2') and the second (5, 5') porous structures are provided in the same layer/coating of the porous material.

5. Porous material for catalytic conversion of exhaust gases according to claims 2 or 3, characterized in that the first (2, 2') and the second porous structures (5, 5') are provided in different layers/coatings of the porous material.

6. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-5, characterized in that the carrier with the second porous structure (5, 5') has been adapted to molecule size and/or adsorption properties of the reducing agent (HC).

7. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-6, characterized in that the ratio between oxidation catalyst (OX) and reduction catalyst (RED) has been optimized so that the production of nitrogen dioxide (NO<sub>2</sub>), according to the first reaction (3), essentially corresponds to the consumption of nitrogen dioxide (NO<sub>2</sub>), according to the third reaction (6).

8. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-7, further comprising a first portion (10) and a second portion (11), wherein the first portion (10) is intended to receive the exhaust gases (12) before the second portion (11) during the catalytic conversion,

characterized in that the first portion (10) contains a larger quantity of the oxidation catalyst (OX) than the second portion (11), whereas the second portion (11) contains a larger quantity of the reduction catalyst (RED) than the first portion (10).

9. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-8,

characterized in that the first (2, 2') and/or the second (5, 5') porous structure is provided in a carrier which is a zeolite crystal structure.

10. Porous material for catalytic conversion of exhaust gases according to claim 9,

characterized in that the porous material comprises a first zeolite (14), providing the first porous structure (2, 2'), and a second zeolite (15), providing the second porous structure (5, 5').

11. Porous material for catalytic conversion of exhaust gases according to claim 10,

characterized in that the porous material comprises a physical mixture (13) of the first zeolite (14) and the second zeolite (15).

12. Porous material for catalytic conversion of exhaust gases according to claim 10,

characterized in that the porous material comprises a layered structure (16, 17) of the first zeolite (14) and the second zeolite (15), wherein said first and

second zeolites (14, 15), depending on the expected composition of the exhaust gases (12) which are to be catalytically converted, have been arranged in relation to each other in said layered structure (16, 17), preferably so that the second zeolite (15) will encounter the exhaust gases (12) before the first zeolite (14) during the catalytic conversion.

13. Porous material for catalytic conversion of exhaust gases according to claim 10, characterized in that the second zeolite, providing the second porous structure (5, 5'), has been applied by over-growth onto the first zeolite, providing the first porous structure (2, 2').

14. Porous material for catalytic conversion of exhaust gases according to anyone of claims 10-13, characterized in that the content of oxidation catalyst (OX) has been reduced in outer layers (8) of the first zeolite by means of regulating penetration depth and/or dispersion.

15. Porous material for catalytic conversion of exhaust gases according to any one of claims 10-14, characterized in that an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) has been crystallized onto the crystal structure of the first zeolite.

16. Porous material for catalytic conversion of exhaust gases according to any one of claims 10-15, characterized in that the crystal structure of the first zeolite comprises crystal grains having a grain size (9) and a shape which has been optimized both in order to prevent access for the reducing agent (HC), and in order to allow effective oxidation of NO to NO<sub>2</sub>.

17. Porous material for catalytic conversion of exhaust gases according to any one of claims 10-16, characterized in that the first zeolite is a Ferrierite-zeolite or a Chabazite-zeolite.

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18. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-14, characterized in that the reducing agent (HC), which is at least partially consumed according to the third reaction (6), is a hydrocarbon ( $H_xC_y$ ) and/or a chemical compound ( $H_xC_yO_zS_w$ ) further comprising oxygen/and or sulphur.

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19. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-18, characterized in that the reduction catalyst is an acidic zeolite catalyst.

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20. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-19, characterized in that the reduction catalyst (RED) comprises Brönstedt acid sites, silver (Ag), copper (Cu), Rhodium (Rh), Indium (In), Iridium (Ir), or combinations of these.

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21. Porous material for catalytic conversion of exhaust gases according to any one of the preceding claims, characterized in that the oxidation catalyst (OX) comprises platinum (Pt) and/or palladium (Pd).

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22. Porous material for catalytic conversion of exhaust gases according to any one of the preceding claims, characterized in that the first or/and the second porous structure is/are provided in carriers attached to a substrate (18).

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23. Method for catalytic conversion of exhaust gases, comprising oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO<sub>2</sub>) over an oxidation catalyst (OX), according to a first reaction (3), whereby said oxidation catalyst (OX) also has the ability to, according to a second reaction, catalyse oxidation of a reducing agent (HC),

characterized in that the reducing agent (HC) is sterically prevented (4, 4') from coming into contact with the oxidation catalyst (OX), as a result of which primarily the first reaction (3), out of said first and second reactions, takes place over the oxidation catalyst (OX).

24. Method for catalytic conversion of exhaust gases according to claim 23, further comprising a third reaction (6) over a reduction catalyst (RED), wherein nitrogen dioxide (NO<sub>2</sub>), in the presence of a reducing agent (HC), is reduced into nitrogen (N<sub>2</sub>),

characterized in that the reducing agent (HC) participates in the third reaction (6) and thereby is at least partially consumed, in order to provide catalytically converted exhaust gases (12') having a reduced content of nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>) and the reducing agent (HC), and a proportionately low content of dinitrogen oxide (N<sub>2</sub>O) and/or carbon monoxide (CO).

25. Method for catalytic conversion of exhaust gases according to claim 23 or 24,

characterized in that an additional amount (19, 19', 19'') of reducing agent (HC) is added before reduction takes place over the reduction catalyst (RED), according to the third reaction (6).

26. Method for catalytic conversion of exhaust gases according to claim 25,

characterized in that the additional amount (19, 19', 19'') of reducing agent (HC) is regulated on the basis of a measured or previously mapped content (20) of reducing agent (HC) and/or nitrogen oxides ( $\text{NO}_x$ ) in the exhaust gases (12, 12').

27. Method for catalytic conversion of exhaust gases according to claim 26,

characterized in that the measured content (20) of reducing agent (HC) or nitrogen oxides ( $\text{NO}_x$ ) in the catalytically converted exhaust gases (12') is used in a diagnostic control system (22) as a measure of the status of the catalytic conversion.

28. Method for catalytic conversion of exhaust gases according to any one of claims 23-27,

characterized in that the exhaust gases (12), before oxidation over the oxidation catalyst (OX) according to the first reaction (3), are passed through a device having the ability to store and when necessary release nitrogen oxides ( $\text{NO}_x$ ).

29. Method for catalytic conversion of exhaust gases according to any one of claims 23-28,

characterized in that the exhaust gases (12), before oxidation over the oxidation catalyst (OX) according to the first reaction (3), are passed through a device having the ability to store and when necessary release reducing agent (HC).

30. Method for catalytic conversion of exhaust gases according to any one of claims 23-29,

characterized in that the temperature of the exhaust gases is regulated (23) in order to be within an

active temperature interval of the oxidation catalyst (OX) and/or the reduction catalyst (RED).

5 31. Method for catalytic conversion of exhaust gases according to any one of claims 23-30,  
c h a r a c t e r i z e d i n that the at least partially catalytically converted exhaust gases, after (21) oxidation over the oxidation catalyst (OX) and reduction over the  
10 reduction catalyst (RED), are allowed to pass a second oxidation catalyst (24) over which oxidation of residues of reducing agent (HC) and/or carbon monoxide can take place.

32. Method for catalytic conversion of exhaust gases according to any one of claims 23-31,  
15 c h a r a c t e r i z e d i n that the exhaust gases (12) originate from an internal combustion engine (25), and that the reducing agent (HC) comprises a hydrocarbon ( $H_xC_y$ ) and/or a chemical compound ( $H_xC_yO_zS_w$ ) further containing oxygen/and or sulphur.

20 33. Method for catalytic conversion of exhaust gases according to claim 32,  
c h a r a c t e r i z e d i n that both the fuel (26) consumption of the internal combustion engine (25),  
25 influencing the chemical composition of the exhaust gases (12), and the residue content of nitrogen oxides ( $NO_x$ ) in the catalytically converted exhaust gases (12') are regulated in order to fulfil relevant legislative regulations.

30 34. Method for catalytic conversion of exhaust gases according to claim 32 or 33,  
c h a r a c t e r i z e d i n that the internal combustion engine (25) is a diesel engine and that the  
35 reducing agent (HC) originates from internal combustion in said diesel engine.



35. Method for catalytic conversion of exhaust gases according to claim 34,

characterized in that an additional amount (19) of reducing agent (HC) is added via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

36. Use of a porous material, according to any one of claims 2-22, providing functions both for the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO<sub>2</sub>) and for the reduction of nitrogen dioxide (NO<sub>2</sub>) into nitrogen (N<sub>2</sub>), for catalytic conversion of exhaust gases (12) which have an oxygen surplus.

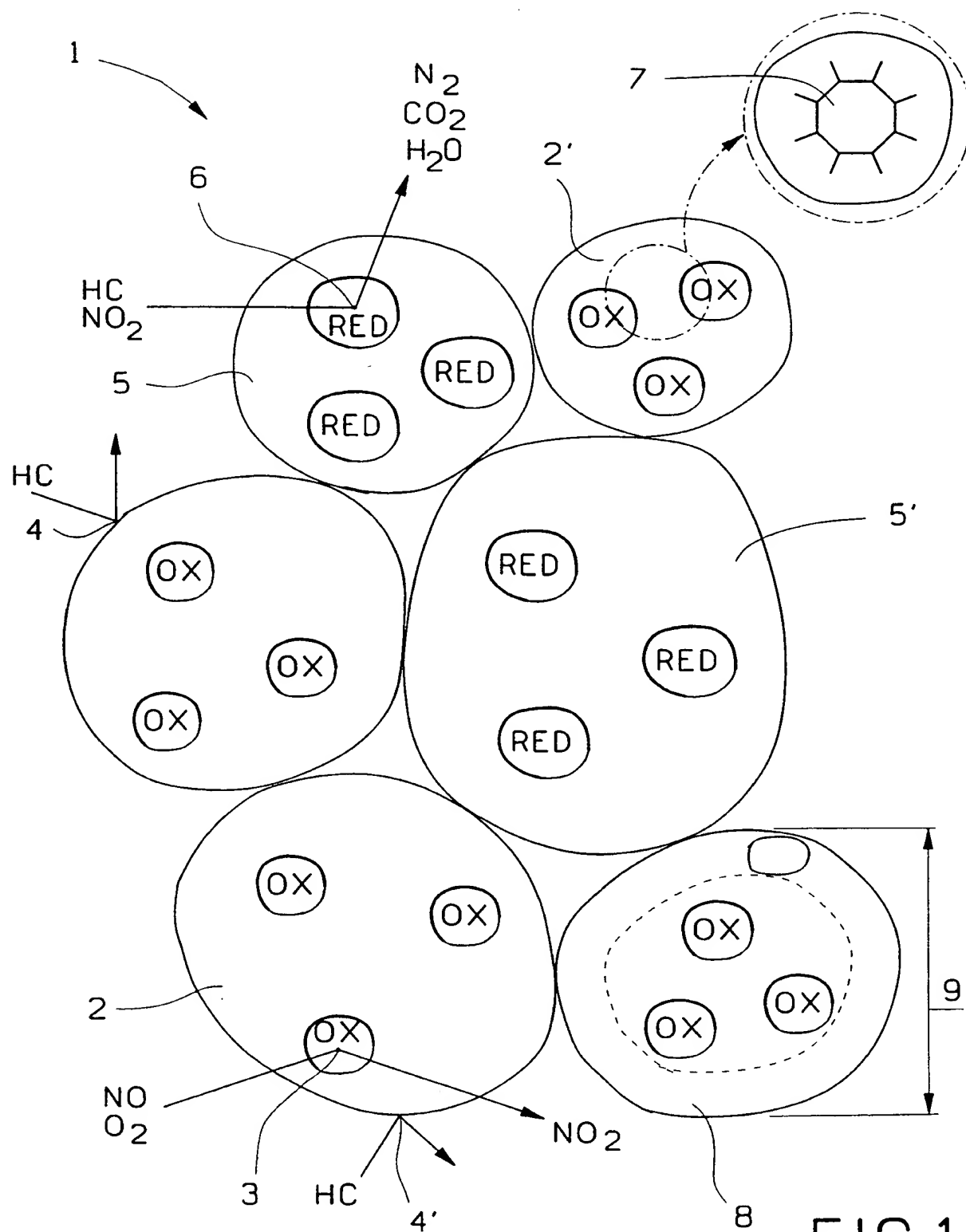
37. Arrangement for catalytic conversion of exhaust gases, whereby said exhaust gases (12) originate from an internal combustion engine (25),

characterized in that the arrangement comprises a porous material (1) according to any one of claims 1-22.

38. Arrangement for catalytic conversion of exhaust gases according to claim 37,

characterized in that the arrangement operates through a method according to any one of claims 23-35.

1/7

FIG.1

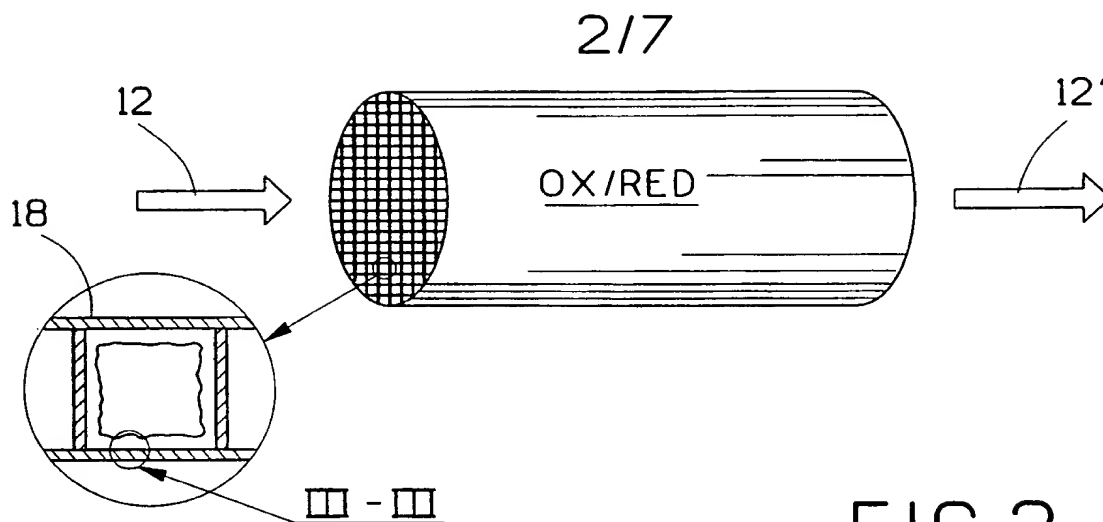


FIG. 2

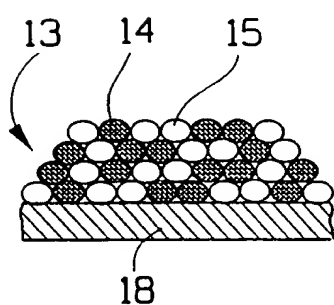


FIG. 3A

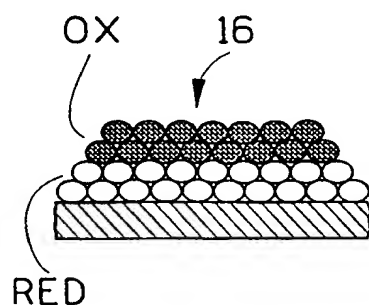


FIG. 3B

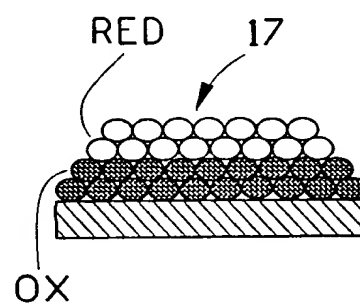


FIG. 3C

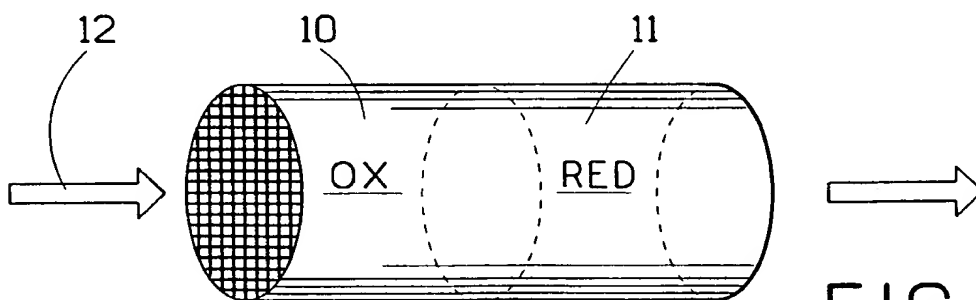


FIG. 4A

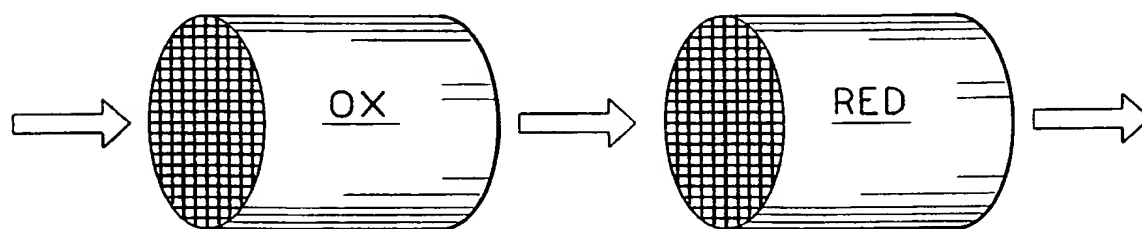


FIG. 4B

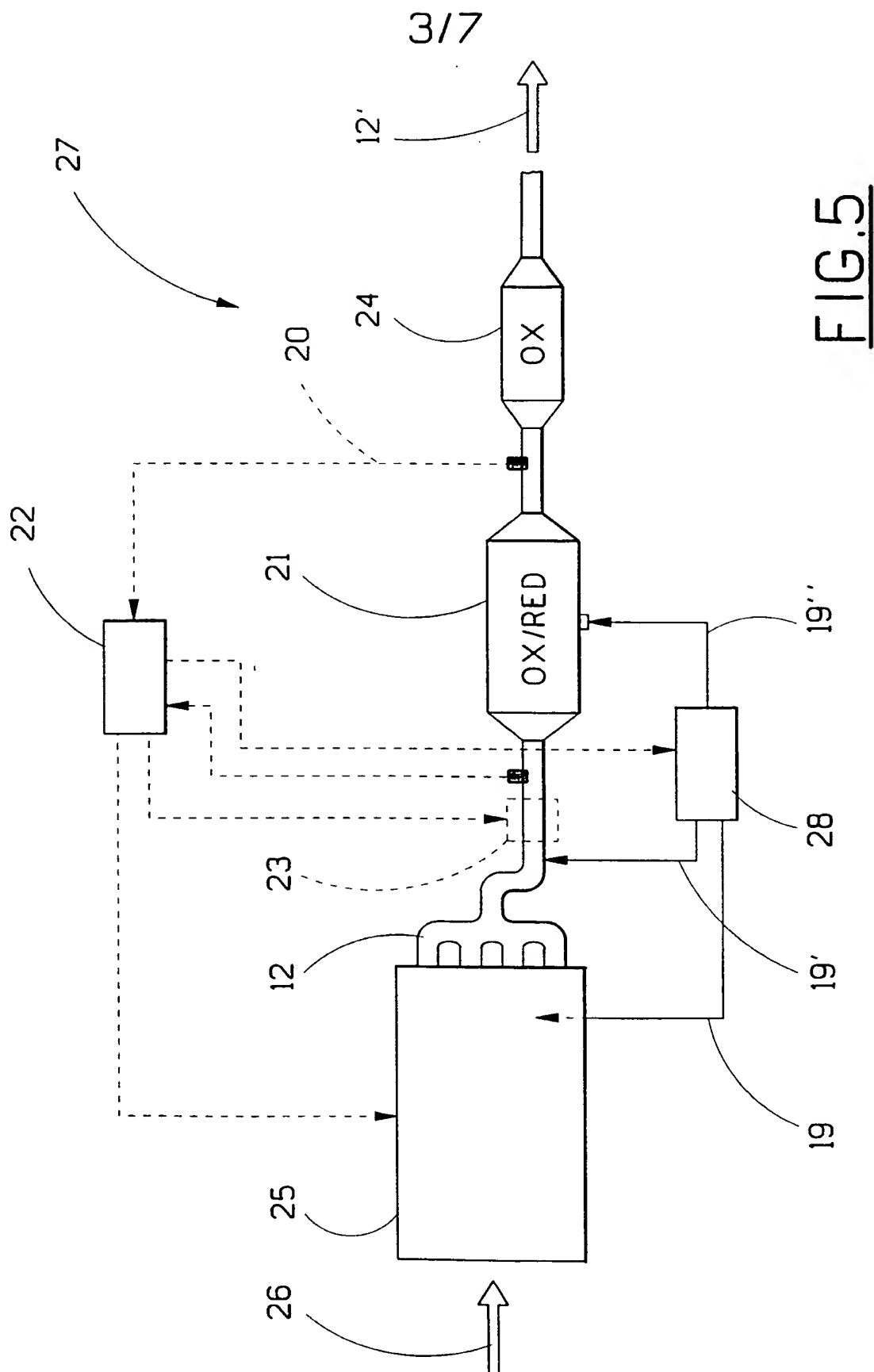
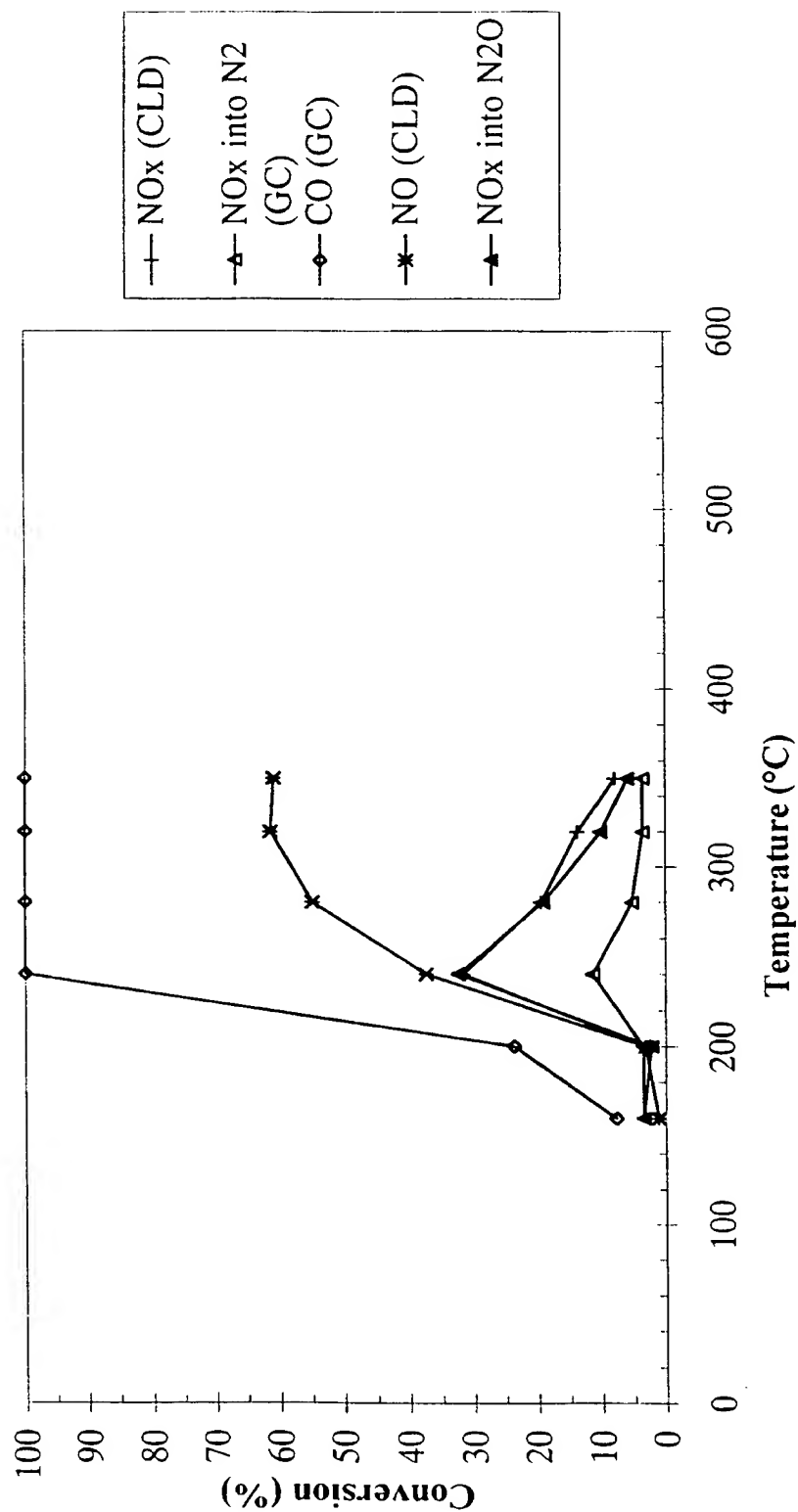


FIG. 5.

4/7

**Graph 1A**

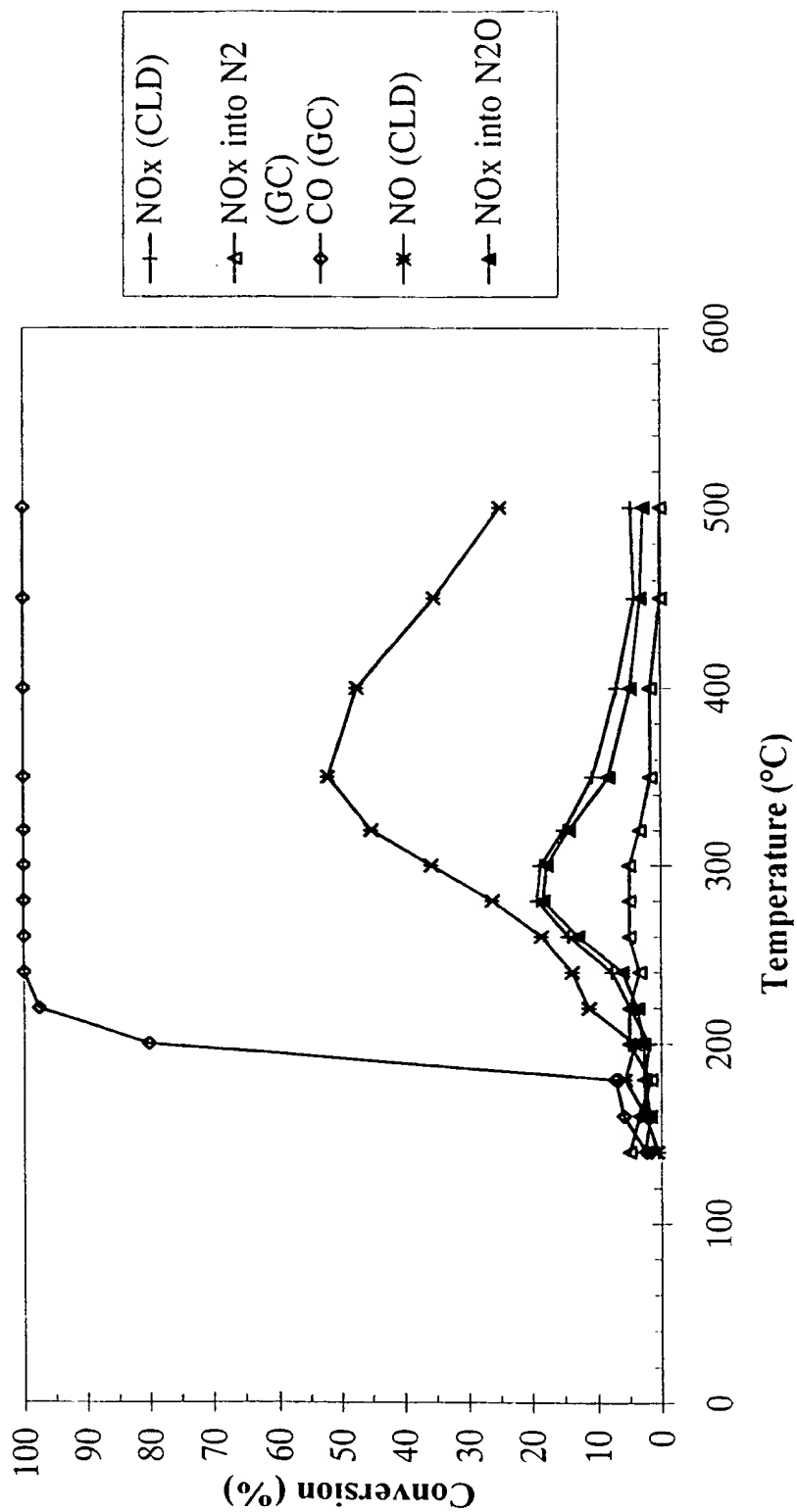
0.5wt% Pt-FER/5wt% Ag-FER (COK-Si/Al=6) (30/70)  
(350 ppm C<sub>8</sub>H<sub>18</sub>, 500 ppm NO, VHSV = 60,000 h<sup>-1</sup>)



5/7

**Graph 1B**

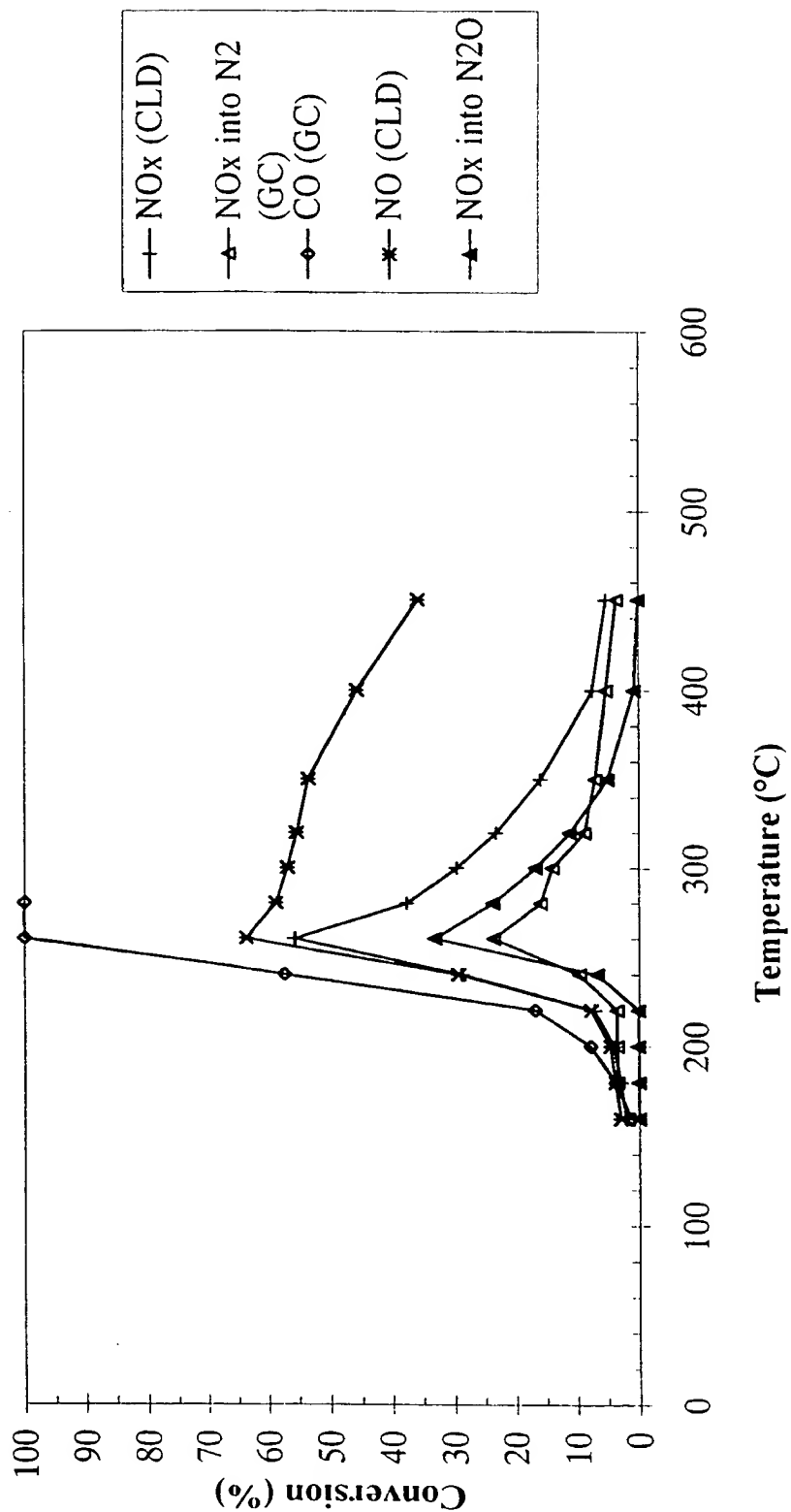
0.5wt% Pt-FER/5Wt% Ag-FER (COK-Si/Al=6) (30/70)  
(350 ppm isoC<sub>8</sub>H<sub>18</sub>, 500 ppm NO, VHSV = 60,000 h<sup>-1</sup>)



6/7

**Graph 2A**

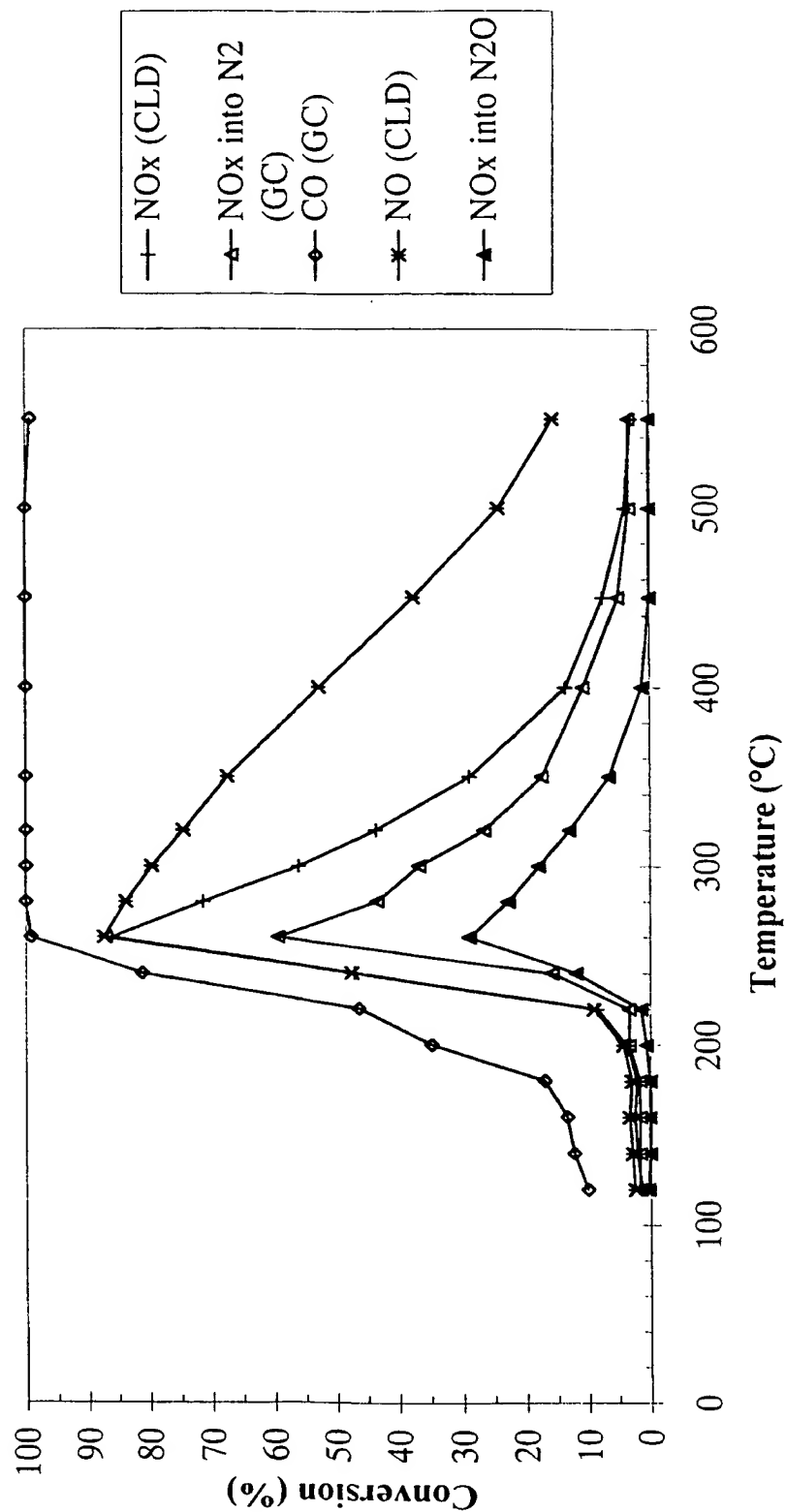
0.5wt% Pt-FER/5Wt% Ag-MOR (30/70)  
(350 ppm C<sub>8</sub>H<sub>18</sub>, 500 ppm NO, VHSV = 60,000 h<sup>-1</sup>)



7/7

**Graph 2B**

0.5wt% Pt-FER/5Wt% Ag-MOR (30/70)  
(350 ppm isoC<sub>8</sub>H<sub>18</sub>, 500 ppm NO, VHSV = 60,000 h<sup>-1</sup>)





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/02067

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01D 53/94, F01N 3/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01D, F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9749480 A1 (IVANOV A A ET AL), 31 December 1997 (31.12.97), abstract --	1
A	EP 0682975 A1 (KABUSHIKI KAISHA RIKEN), 22 November 1995 (22.11.95), claim 1, abstract --	1
A	US 3901821 A (WILLIAM B. RETALLICK), 26 August 1975 (26.08.75), abstract --	1
A	EP 0445408 A1 (BAYER AG ET AL), 11 Sept 1991 (11.09.91), claim 1 --	1

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

14 July 1998

Date of mailing of the international search report

22-07-1998

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/02067

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0499931 A1 (BAYER AG ET AL), 26 August 1992 (26.08.92), claim 1  --	1
A	US 5465574 A (THOMAS T. MA), 14 November 1995 (14.11.95), abstract  -- -----	1

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Information on patent family members

30/06/98

International application No.

PCT/SE 97/02067

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